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"The thermic method of vitrification of the radioactive pulps and the safe disposal problem of vitreous preparations".

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Expediency of treating highly radioactive wastes into solid vitreous preparations suitable for final disposal is now generally recognized. Although heat treatment of wastes is evidently a promising method its industrial application considerably lags behind research work. In large part this lag is due to the difficulty of developing high-efficiency, continuously acting apparatuses and plants suitable for the radiochemical industry and burial-grounds having simple construction and safe in the exploitation.

Specific requirements of the radiochemical industry limit the application of the equipment used in other branches of industry. Therefore, the aim of the present investigation was to develop a continuous process and technological equipment for heat treatment of radioactive pulps and also creation of burial-grounds for disposal of solid molten preparations of high activity.

The process development was conducted in application to hydroxide pulps obtained as a result of alkaline precipitation of hydroxides of iron, chromium, manganese, calcium and other elements from nitric acid radioactive wastes.

The technological process for heat treatment of radioactive pulps includes the following main stages:

1) Dehydration of pulp and calcination of its solid residue.
2) Mixing of pulp solid residue with flux.
3) Preparation of vitreous melt.
4) Pouring of vitreous melt.

I. Fundamentals of technology for heat treatment of radioactive pulps

We selected the fluidized bed method for dehydration and calcination of radioactive pulps. The application of the fluidized bed permits to carry out the dehydration with high rates. The use of solid residue of hydroxide pulp itself as a fluidized bed material is not to the purpose, since close by magnitude values of fluidization (0.15 m/sec) and of entrainment (0.35 m/sec) necessitate considerable reduction of fluidization operating velocity range and lead to increased entrainment of fluidized bed material from the apparatus.

The indicated reason necessitated the use of an inert material. For this purpose we have selected quartz sand with particle size of 0.4 and 0.7 mm.

1. The use of quartz sand with d = 0.4 mm permits to increase the operating velocity of fluidization to 1 m/sec and the use of sand with d = 0.7 mm - to 1.5 m/sec.

2. Quartz sand, getting subsequently into the burden, does not change physico-chemical properties of molten preparation since for the subsequent process of vitreous melt preparation quartz sand is being introduced into the burden as a glassforming component.

3. Quartz sand is heat stable at operating temperatures (500-700 °C) in the reaction zone and is chemically inert, in these conditions, to the pulp solid residue, and to the apparatus material.

As a fluidizing agent, gas (air) or superheated steam can be selected. The temperature of the fluidizing agent is determined by the operating temperature of dehydration and calcination. Operating velocities of fluidization can be attained both by means of gas (steam) fed to the fluidization and by means of the vapour phase formed in the apparatus during dehydration of the pulp. The use of superheated steam permits to reduce considerably volumes of gases subject to purification.

Completeness of dehydration and calcination of the pulp

solid residue is determined by the residence time of solid residue particles in the reaction zone of the apparatus with the fluidized bed. Conducted studies showed the ability of sand fluidized bed to retain fine-dispersed (1-5 μ) particles of the solid residue to complete dehydration of the material. It was found that residence time of particles in the fluidized bed depends on nature of the material, specific surface of the fluidized bed and varies in wide range. The main part of solid residue particles stays in the fluidized bed 3-5 min.

Lack of chemical interaction between the fluidized bed material and the pulp solid residue favours its complete carrying out from the apparatus by the gas-vapour flow owing to great difference in values of entrainment velocity of particles of fluidized bed material ($\sim$ 2,5 m/sec) and entrainment velocity of solid residue particles (0.35 m/sec).

The difference in entrainment velocities of particles of the fluidized bed and the solid residue can be used for unloading the solid residue from the apparatus followed by its subsequent separation from the gas-vapour phase in the cyclone. Separation of the solid residue in the cyclone is favoured by coarsening of its particles in the process of dehydration in the fluidized bed with the formation of conglomerates having size of 20-40 μ. The resulting conglomerates are unstable and the bulk of them disintegrates on feeding the powder to the smelting apparatus with the formation of more fine fractions.

To provide high efficiency of the present process it is necessary to develop a continuous process for the preparation of the melt. One of the main problems is the selection of flux composition and a method of its introduction into the smelting zone. Studies conducted showed the expediency of using natural minerals (ulexite albite and oth.) for introduction of compounds of boron, silicon and sodium into the burden. In the burden prepared on the base of such minerals the liquid phase emerges at temperature above 800°C and thus it is possible to avoid the formation of crusts in pipe lines at the top of the smelting apparatus. On heating the indicated burden to 1100°C a vitreous melt is formed suitable for its unloading

from the apparatus. In order to prepare the homogeneous melt it is necessary to keep it in the reaction zone for about 2 hours. Studies showed that the method of the burden loading into the continuously acting smelting apparatus and the burden dispersity are also of great importance. To reduce the time required for the preparation of the homogeneous melt it is expedient to use fine-dispersed materials and to load the burden on the melt surface by small portions corresponding to 0.2 g/cm^2·min. On the other hand, the use of fine-dispersed materials can cause increased entrainment of the burden particles by back gas flows formed as a result of the decomposition of the burden components which are heat unstable at these temperatures. The entrainment of fine-dispersed particles of the burden can be reduced by means of complete thermal decomposition of unstable compounds of the hydroxide pulp solid residue in the stage of dehydration and calcination and by using precalcined materials as fluxes.

When introducing fine-dispersed flux materials the formation of crusts in the apparatus and pipe lines occurs owing to the formation of a liquid film on contact of particles with heated sections of the surface followed by sticking of solid residue particles to these surface sections. The indicated phenomenon has the highest intensity on surface sections heated to 700-900°C. By using a pelletized flux it is practically possible to avoid the formation of crusts in pipe lines. The procedure for unloading of the prepared homogeneous melt is determined by the time of complete melting and by the capacity of the selected smelting apparatus.

For experimental verification of the obtained data a model-pilot plant was created, the line diagram of which is shown in fig. 1. The design of apparatuses of the model-pilot plant was developed by a group of coworkers under the guidance of V. T. Shatsillo, L. I. Chechetin and L. D. Kosenko.

The pilot plant consists of the following main apparatuses:

1) vessel for the starting material;
2) proportioning pump for pulp feeding;
3) apparatus with the fluidized bed;
4) steam superheater;
5) cyclone;

6) flux dosing apparatus;
7) smelting apparatus;
8) vessel for the melt;
9) purifying facilities.

As was already indicated, a hydroxide pulp with concentration of the solid phase 10-100 g/l was used as a starting material.

Feeding the pulp to dehydration was accomplished by means of a proportioning pump and three low pressure pneumatic spraying injectors of the Shuhov system.

In this case the pulp flow rate was from 10 to 30 l/hr with air consumption for spraying the pulp being about 0.2 Nm^3/hr·l. Dehydration and calcination of the pulp was accomplished in the apparatus with the fluidized bed which represents a column having the internal diameter of 250 mm and the height of about 2000 mm. In the upper part of the apparatus there is an expander with the internal diameter of 400 mm. Along its height the apparatus is divided into two parts: the upper and the lower parts. The lower part of the apparatus is a gas-feed chamber fitted with a gas-distributing grate.

Removal of the fluidized bed material from the apparatus was accomplished through its bottom. The upper part of the apparatus includes the zone of dehydration and calcination of the starting material (the pulp) and is fitted with three injectors located in one horizontal plane at the level of ~ 150 mm from the gas-distributing grate.

The apparatus zone for dehydration and calcination is provided with heating. We have tested three types of heating the apparatus with the fluidized bed (see fig.2, 3, 4):

1. Heating by means of 7 vertically located tubular electric heaters, evenly distributed from each other (18-20 mm) over the section of the apparatus. Power input on each electric heater was continuously adjusted and did not exceed 8 kW.

2. Heating by means of 18 electric heaters located horizontally at a distance of 15 mm from each other. Power input on each electric heater did not exceed 3.2 - 3.8 kW.

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3. Heating the apparatus walls by means of high-frequency currents. Power supply for induction heaters was fed from 100-kW generator with frequency 2500 c.p.s. The types of heating, tested by us, provided the heating of sand fluidized bed to 700°C, temperature drop in the space of the fluidized bed not exceeding 100°C. Specific power consumption was 1.5 - 1.8 kWhr per 1 cubic metre of the pulp.

The charge of sand into the apparatus did not exceed 15 kg. To maintain quartz sand in the state of fluidization, air and superheated steam at 600°C were used. The average consumption of the fluidizing agent was about 40 kg/hr. For separating solid and gas-vapour phases a cyclon heated to 400-500°C was used to avoid vapour condensation and associated sticking of the solid residue particles to the cyclone walls. The degree of purification in the cyclone is 85-90%. The solid residue separated in the cyclone was mixed in the flow with the flux and was fed to the furnace for melt preparation.

The smelting apparatus is divided along its height into two parts. The upper part with capacity of ~ 20 l is designed to prepare the melt and is fitted with the device for loading the burden on the melt surface. The lower part is a facility for proportioning and unloading of the prepared melt from the apparatus. Unloading of the melt from the apparatus is performed owing to overflow of the low-viscosity melt through the bottom feeder.

The mode of feeders operation is based on freezing the effluent melt flow by means of cooled air. The air consumption for freezing the feeders was about 6 N m^3/hr.

Two methods of heating the smelting apparatus were tested: (See fig. 5, 6)

1) heating by means of 6 horizontally located tubular electric heaters with total power of 7.5 kW;

2) heating of the smelting apparatus body by means of high-frequency currents (2500 c.p.s.). Total power of the induction heater was about 10 kW. The tested types of heating provided continuous adjustment of temperature in the reaction zone to 1200°C.

Pouring of the prepared melt was performed every 2-3 hours. The power consumption for the melt preparation was 7.5 - 10 kWhr. The efficiency of the smelting apparatus achieved to 6 kg/hr. After separation of the solid residue in the cyclone gas-vapour phase and the part of the solid residue, got through with it, were fed into the system of vapour phase condensation and off-gases purification. In the course of operation of the apparatus with the fluidized bed abrasion of quartz sand granules was observed, and a part of them was entrained into the cyclone in the amount of about $5 \cdot 10^{-2}$ g/kg·hr.

Consumption factors and standards of the technological process given above are the average ones for every 500 hours of operation. Work conducted on the model-pilot plant showed the feasibility of realizing the continuous process for heat treatment of radioactive pulps. One of the main difficulties in solving this problem lies in ensuring process stability and consistent operation of separate apparatuses. The flowsheet and details of the apparatus for process are deecribed not only in our paper.

The fundamental results flowsheet and details of the apparatus required for the drying and vitrification of radioactive sludge by means of gas and heat-remover, was published by N.E.Brezhneva et al. on the symposium in Vienna /1/.

Possible variants of burial-ground for disposal of solid molten preparations of high-activity

Particular attention is given to study of chemical stability of glass-like preparations and solution of thermal problems in the design of "burial-grounds", when choosing fission fragments. Considerably less attention is given to changes in preparation properties induced by ionizing radiation /2-5/. At the same time it is shown /3/ that ionizing radiation destroys the surface of a preparation and increases its solubility. This may be explained by the presence of surface radiation-induced chemical reactions of molten preparation with air components. Changes in preparation characteristics may also arise under prolonged action of high temperatures. /1,3/.

A temperature increase is known to occur due to energy

release during radiation-induced decomposition of any concentrates containing radioisotopes. Heat release and self-heating are of particular significance in the burying of radioactive wastes. It was shown earlier /2 / that heating of solid fission-produced concentrates may reach considerable values even for single blocks because of the high specific activity and worse heat-transfer compared with liquids. This must be taken into account in studies on properties of molten preparations.

Examining a preparation surface by means of a microscope (fig.7) has shown sharp lowering of the radiation induced decomposition rate with increasing temperature. The change in the surface structure is, in fact, inappreciable above 1500°C. No decrease in chemical stability connected with structure changes of the irradiated surface was observed above this temperature (fig. 8).

The radiation-induced effect on properties of molten preparations liable to high temperature crystallization, becomes perceptible at a temperature above 600°C. X-ray investigations have shown that the preparations irradiated at this temperature are crystallized easy compared with non-irradiated samples.(Fig.9).

Studies on relaxation properties of fused preparations have shown /3/ that at 500°C marked decrease in their structural viscosity.

Obviously, the energy necessary for atom displacement at lower structural viscosity decreases to such an extent that the cascade displacement by irradiation becomes possible. In this case no temperature annealing of radiation-induced is defects is observed, due to transition of the system from a metastable (vitreous) to a thermodynamically more stable (crystalline) state.

Investigations have shown that radiation-induced chemical destruction of glass blocks may be prevented by creating higher temperatures (not lower than 150°C) in the disposal. This is especially necessary within the first months after charge of the disposal when the specific activity of wastes is and, consequently, the radiation-induced chemical decompositions rate are highest. The second problem when designing a burial-ground is a minimum contact of the preparation with air as destruction takes place owing to the occurrence reactions with air components.

Naturally, of great importance will be the correct estimation of temperature peaks which are likely to arise in a disposal and will be dependent upon both the specific heat release of buried material and heat removal. Knowledge of the thermophysical constants of a preparation is necessary for solution of this problem. It was shown earlier /2,6/ that the thermal conductivity coefficient for fused fission-reduced preparations was 1,1 kcal/m.h.°C. However, a disordered drop of blocks and their storage in heaps is most desirable for simplification of charge technique. Thus when estimating the heat transfer the term "pure" is not adequate for the thermal conductivity coefficient as it is necessary also to consider the thermal conductivity of block casements, the air convection in gaps and the thermal emission (for rather high temperatures). Therefore it is advisable to consider the layer of samples as a coarse-grained material and to use provisionally the definition thermal conductivity coefficient of a heaped layer. To determine this value, measurements were made of the temperature difference in layers consisting of ampoules with molten preparations (specific activity from 2 000 to 10 000 curie/l). The apparatus for measurements (fig. 10) was located in a protective chamber. 100 ampoules of 20 ml each containing molten preparations were placed into the apparatus. The preparations were obtained from wastes at different time delay: 55 ampoules (lower layer), 30 ampoules (middle layer) and 25 ampoules (upper layer). Apparatus for thermal modelling, containing ampoules with non-radioactive preparations were designed in order to obtain more accurate data. Electric heaters were adjusted inside the ampoules.

Fig. 11 shows the results of determinations of temperatures for the heating of layers in the apparatus. The data obtained permitted determination of the "thermal conductivity coefficient" for a heaped layer. This value did not differ, in fact, from the monolith thermal conductivity coefficient under experimental conditions and was found to be 0.9 to 1.1 kcal/m.h.°C. The expected decrease in the thermal conductivity coefficient due to presence of air gaps between ampoules was not observed mainly owing to presence of the heat conducting metal casement in the burial-ground.

In constructing burial-grounds considerable attention

attention should naturally be given to ensuring highest compactness and to absence of special cooling agents used for heat-removal. The critical excess temperature of any heat releasing product is known to be determined not only by the heat release value and thermal conductivity, but also by heat losses to the environment. It involves temperature differences both in the mass of the disposed product and between the product and the environment. Table 1 shows volumes of radioactive preparations stored as a monolith and "in heap" for the case of most intensive heat removal when there is no difference in the temperature of a preparation surface (or a layer) and that of the environment provided the temperature difference in the centre and on the surface of a preparation does not exceed 900°C.

Table 1

Critical sizes of highly active molten concentrates at most intensive heat removal and a maximum temperature of 900°C.

Specific heat release kcal/m^3·h		$9 \cdot 10^4$		$1.6 \cdot 10^4$	
Charge shape of disposal		monolith	in heap	monolith	in heap
Shere	radius, m	0.29	0.29	0.68	0.68
	volume, m^3	0.10	0.05	1.30	0.65
Infinite cylinder	radius, m	0.24	0.24	0.56	0.56
	volume of running meter, m^3	0.18	0.09	0.99	0.49
Infinite plane layer x)	thickness, m	0.16	0.16	0.40	0.40
	volume in m^3 C_2 area, m^2	0.16	0.08	0.40	0.20

x) Values given for unilateral cooling of a plane layer; for bilateral cooling the values must be doubled.

The table shows that the permissible volume of a disposed ration is dependent on its specific heat release (specific activity) and is greatly limited even at strong heat removal from its surface.

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An additional temperature difference between a preparation surface and the environment always takes place in reality. Then the tabular sizes should be decreased, and the decrease should be greater with increasing difference.

Different variants of burial-ground design involving various heat-exchangers are given below:

1. The best heat-removal may be accomplished using flowing cooled water as heat removal agent. In this case the preparation volumes may appear to be close to those in the table. However, a burial-ground with water cooling must have a complex construction and, which is particularly important, must be under continuous control for years.

2. Using air as heat-transfer agent results in an increase in the temperature difference between the preparation surface and the environment and in decrease in tubular sizes. Here best conditions for heat-exchange will take place when the air is blown through a layer of blocks at a higher rate. However, this would require a system for removing radioactive dust by air purification and would create most favourable conditions for radiation-induced destruction of the preparation surface. In using air as a heat transfer agent it is the most advisable to realize heat withdrawal by air streams separated by metal partitions from the preparation-containing ampoules.

3. Temperature control in a burial-ground by means of the endothermic process was shown to be possible /8/. It was suggested that burial-grounds with a molten preparation of high radioactivity be used for fusion of a charge obtained by dehydration of low-active wastes, the m.p. of this charge being by 200-300°C lower than that of highly-active molten materials. First it permits using the heat evolved in the burial-ground and, second, to enclose highly radioactive molten material into a glass-like monolith and thus to protect it against the radiation-induced chemical desctruction and the action of ground waters.

The application of this method is justifiable when there is necessity in disposal of great volumes of low-active, along with highly-active molten wastes.

4. The most simple and cheap type of a burial ground would be one involving no particular cooling agents and constructive materials, i.e. simple placing of the preparation into the ground with subsequent filling up. Table 2 shows the specific volumes of products (per cm^2 of ground surface) which may be buried in ground pits at a maximum temperature of 900°C in the centre of the pit. Calculation is made for pit locations (fig.12). The shape of the volume with preparation-containing ampoules represents a shere of a radius R. This shape was chosen for simplification. Pits are separated by a distance L.

The data obtained are evidence for possible disposal of highly-active fused preparations in earth burial-grounds.

In this case the excess temperature is determined mainly by the difference in temperatures of an ampoule layer surface (e.g. the preparation surface in case of a monolith) and the environment. An increase in the buried preparation volume may become possible by use of soil of a high thermal conductivity (rocky-ground type). Temperature excess in such a burial-ground would not cause destruction of the constructive material (earth) and would only create a heat barrier in the surrounding soil hindering the access of rain and other waters into the burial-ground for several years. From this standpoint it is advisable that the initial temperature be not lower than 500°C.

In filled-up disposals a preparation is reliably protected from atmosphere effects and this creates favourable conditions for protection against radiation-induced destruction.

Taking the value of radioisotope leaching as 10^{-8} g/cm^2 we may draw a conclusion on safe disposal of blocks of a specific activity 10^3 c/l in burial-grounds. Taking into account the sufficiently high sorption capacity of grounds with respect to fission-produced radioisotopes /9/, it is possible to suggest earth burial-grounds for concentrates of higher activity.

Table 2

Permissible sizes of a preparation disposal in burial-grounds

Height of the protective ground layer		2,0 m		2,5 m	
Distance between pits		2 m	3 m	2 m	3 m
Specific heat release $9 \cdot 10^4$ kcal/m^3.h	heaps R	0.29	0.33	0.28	0.32
	heaps $1/m^2$	12.4	8.5	11.8	7.5
	monolith R	0.23	0.27	0.22	0.26
	monolith $1/m^2$	13.3	9.3	11.5	7.9
Specific heat release $1,6 \cdot 10^4$ kcal/m^3.h	heaps R	0.14	0.15	0.13	0.15
	heaps $1/m^2$	1.4	0.8	1.2	0.7
	monolith R	0.11	-	0.11	-
	monolith $1/m^2$	1.6	-	1.4	-

All solid preparations including those involving radioisotopes and glass- and basalt-type preparations are known to be subjected to surface radiation-induced chemical destruction resulting in decreasing mechanical strength of surface layers and in increasing radioisotope solubilities.

In case of preparations intended for disposal of radioactive wastes the rate of radiation-induced chemical processes may be made minimum under the following conditions:

1. Decrease in alkaline and alkaliearth element compounds and boric anhydride in the composition of flux additives or incorporation of transient metals of the Ce type.

2. Providing for temperature in the burial-ground not lower than 500°C during the first years of storage.

3. A limited contact of the preparation surface with air. Thermophysical calculations have shown the possibility of constructing simplest burial-grounds as pits filled up with earth.

Conclusion

It may be considered that with the totality of all works carried out the foundation for realization of process of vitrification in the industry was practically prepared and that it ensures the possibility of creation of safe disposal (burial ground) of highly-active wastes.

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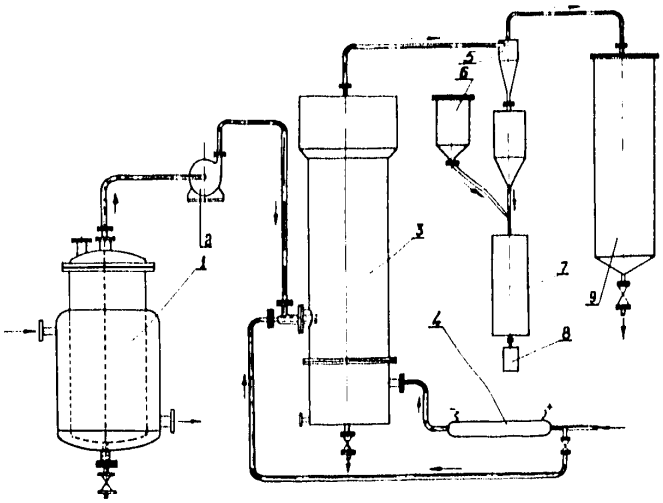

Fig. 1. The line diagram of the modal-pilot plant.

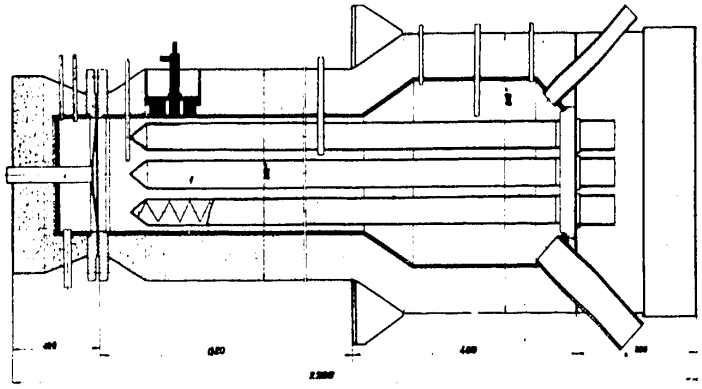

Fig. 2. Heating by means of vertically located tubular electric heaters.

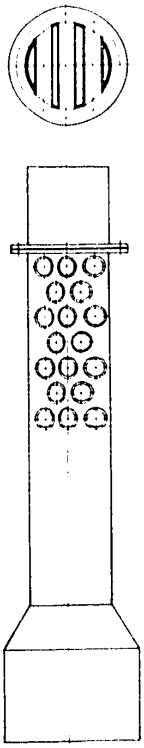

Fig. 3. Heating by means of electric heaters located horizontally.

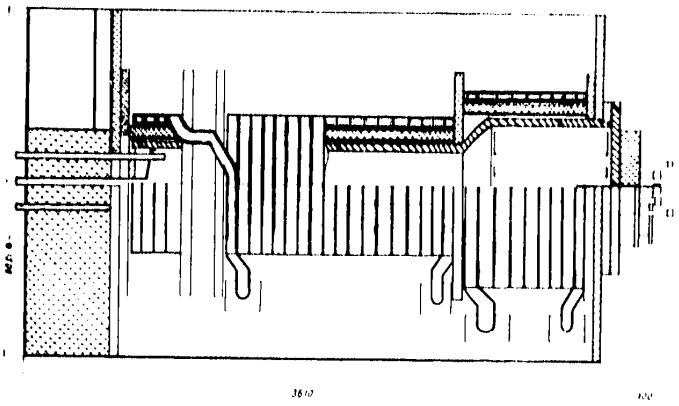

fig. 4. Heating the apparatus walls by means of high-frequency currents.

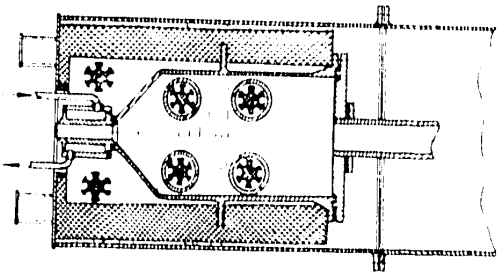

Fig. 5. Heating by means of six horizontally located tubular electric heaters.

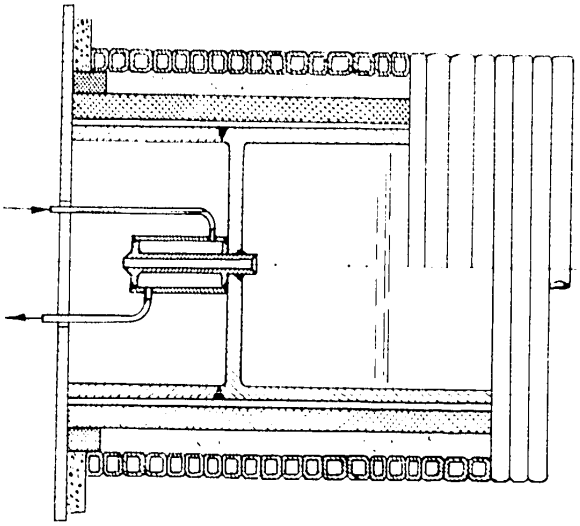

Fig. 6. Heating of the smelting apparatus body by means of high-frequency currents.

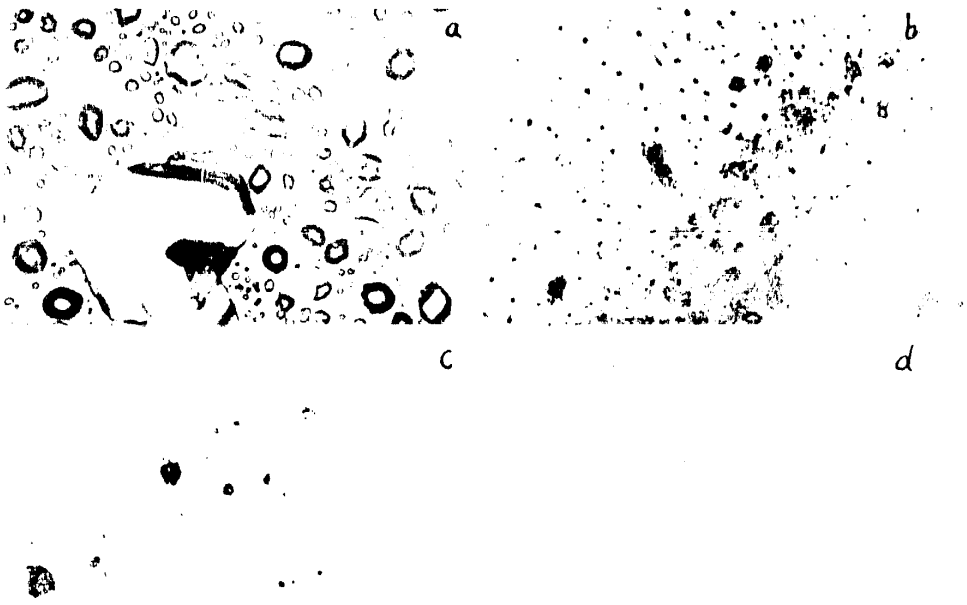

Fig. 7. Change in a molten preparation surface as a result of irradiation from Co^{60} at 20°C (a), 65°C (b), 150°C (c) and 300°C (d) for 240 hours. (x550).

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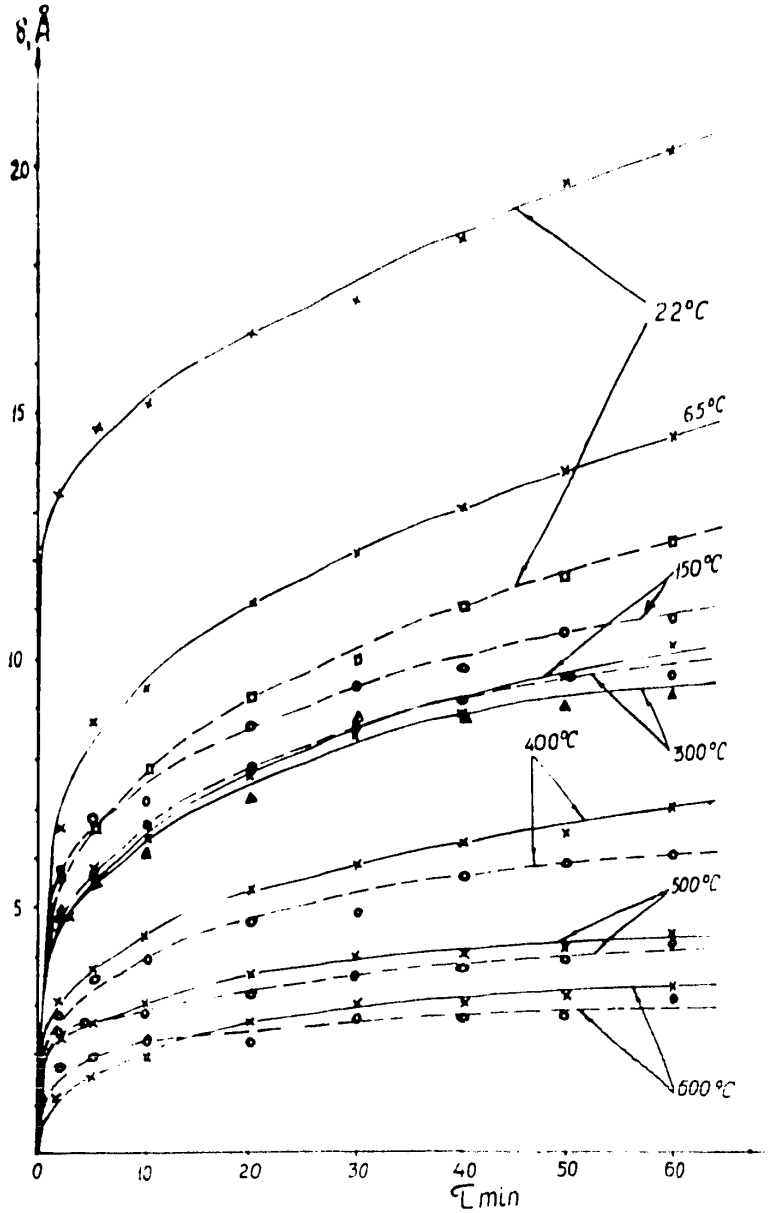

Fig. 8. Change in chemical stability (in the degree of destruction) of a molten preparation containing 35% of SiO_2, 1% of B_2O_3, 3% of CaO and a mixture of aluminium, magnesium, iron and molybdenum oxides as a result of irradiation with Co^{60} at different temperatures.

——— heating and irradiation
– – – – heating without irradiation

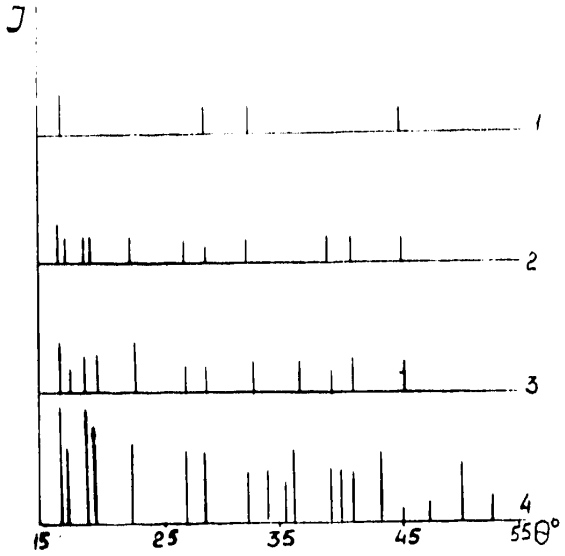

Fig. 9. X-ray pattern of the molten preparation, containing 33% of SiO_2, 10% of MgO, 9% of Al_2O_3, 4% of TiO_2, 3% of CaO, 1% of CaF_2 and a mixture of oxides of elements involved in radioactive wastes before (1) and after annealing for 240 hours without irradiation at 700°C (2) and at 730°C (3) and during irradiation with Co^{60} at 700°C at a dose rate of absorbed energy of 6.10^8 rad.

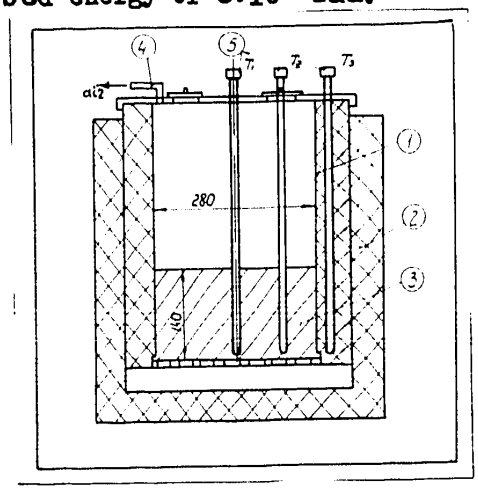

Fig.10. Schematic view of the apparatus used for investigating the rise in temperatures at storing a preparation of high activity.
1. The metal vessels 2. Insulation 3. Volume occupied by preparation-containing ampoules. 4. Blow-line 5. Thermoelectric couple

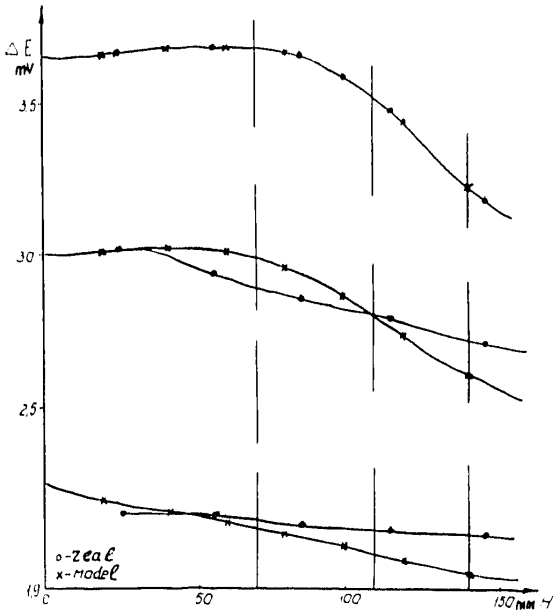

Fig. 11. Results on determination of heat release in a burial-ground containing ampoules for a real and a model preparation.

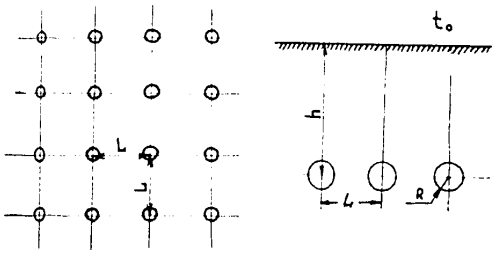

Fig. 12. Schematic calculation of the location of burial-ground pits.

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